

PCT

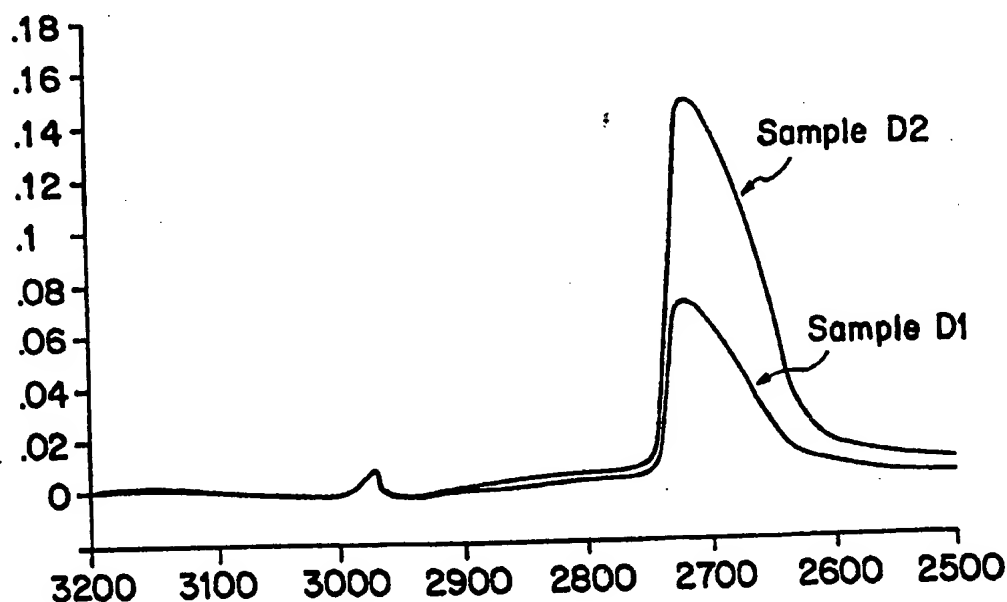
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C03B 20/00, C03C 21/00		A1	(11) International Publication Number: WO 97/32821 (43) International Publication Date: 12 September 1997 (12.09.97)
(21) International Application Number: PCT/US97/03100 (22) International Filing Date: 28 February 1997 (28.02.97) (30) Priority Data: 60/012,881 5 March 1996 (05.03.96) US 60/012,941 6 March 1996 (06.03.96) US (71) Applicant (for all designated States except US): CORNING INCORPORATED [US/US]; 1 Riverfront Plaza, Corning, NY 14831 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): BORRELLI, Nicholas, F. [US/US]; 935 W. Water Street, Elmira, NY 14905 (US). SEMPOLINSKI, Daniel, R. [US/US]; 5 Overbrook Road, Painted Post, NY 14870 (US). SEWARD, Thomas, P., III [US/US]; 614 Euclid Avenue, Elmira, NY 14901 (US). SMITH, Charlene [US/US]; 222 Watauga Avenue, Corning, NY 14830 (US). (74) Agent: HERZFELD, Alexander, R.; Corning Incorporated, Patent Dept., SP FR 02-12, Corning, NY 14831 (US).			(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.

(54) Title: METHOD OF INCREASING THE INITIAL TRANSMITTANCE OF OPTICAL GLASS



(57) Abstract

The invention relates to optical glass having improved initial transmittance, formed by subjecting the glass to a hydrogen and/or deuterium treatment at a temperature, and for a duration of time sufficient to diffuse the hydrogen and/or deuterium into the glass.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France			UZ	Uzbekistan

Accordingly, it is the object of the present invention to produce fused silica glass having improved initial transmittance, and to provide a method for producing such glass.

SUMMARY OF THE INVENTION

5 Briefly, the invention relates to a method of producing glass, particularly fused silica glass, having improved initial transmittance in the UV wavelength region.

In one aspect, the inventive glass is produced by reacting such glass with hydrogen and/or deuterium.

10 In another aspect, the inventive glass is produced by treating glass with hydrogen at such temperature and for a duration sufficient to cause the hydrogen to diffuse into the glass.

BRIEF DESCRIPTION OF THE GLASS

15 Figure 1 shows the subtraction spectra of the reference glass sample (untreated), from those of two deuterium-treated samples;

Figure 2 is a subtraction spectrum of the reference glass sample from a deuterium-treated sample;

20 Figure 3a is a graph comparing the transmittance of an untreated synthetic fused silica glass, with the transmittance of samples of the same glass, treated with deuterium at 350 °C;

Figure 3b is a graph comparing the absorbance spectra of the glasses of Figure 1a;

Figure 4 is a graph comparing the infrared spectra of untreated glass with those of two samples treated with deuterium;

25 Figure 5 is a graph of the change in absorbance versus the parts per million (ppm) by weight OD formed; and

Figures 6a and 6b compare the absorbance spectra of untreated glass with those of the same glass treated after treatment with hydrogen at 600 °C.

DETAILED DESCRIPTION OF THE INVENTION

We have observed that hydrogen treatment of optical glasses resulted in

METHOD OF INCREASING THE INITIAL TRANSMITTANCE OF OPTICAL GLASS

FIELD OF THE INVENTION

The invention relates to optical glass having high initial transmittance in the ultraviolet spectral region. This inventive glass is particularly useful as an optical material for optical applications in the deep ultraviolet region.

BACKGROUND OF THE INVENTION

In the past, it has been suggested that the resistance of fused silica to laser damage can be improved by treating such glass with hydrogen. The treatments of these previous reports are intended to cause impregnation of high concentrations of molecular hydrogen into the fused silica as the degree of laser damage resistance in such samples is said to be related to the amount of molecular hydrogen doped into the glass. The effect of high concentration of the molecular hydrogen on laser damage resistance in fused silica is reported in numerous publications for example, in JP - Hei 6[1994]-166552; JP-Hei6[1994]-166528; JP-A-1-201664; JP-A-6-48734; JP-A-6-24979; JP-A-6-53593; U.S. Pat. 5,410,428; U.S. Pat. 3,220,814; and in co-pending, co-assigned US serial no. 08/422,104.

If fused silica is to be used as an optical material in optical applications in the deep UV, the internal transmittance of the glass at the use wavelengths must be as high as possible. For example, in applications such as lenses for microlithography stepper cameras, where the total path length in glass may be in the 20-50 cm range, an increase in transmittance of 0.01 %/cm is significant.

increased transmittance of the glass in the UV wavelengths. In order to better understand how initial transmittance can be affected by hydrogen, this work was then repeated using deuterium. Deuterium was used for the experiments to obtain spectroscopic evidence for the mode of action of hydrogen.

5 Low UV transmittance of fused silicas can in many cases be related to the presence of impurity metal ions and their charge compensating non-bridging oxygen ions in the glass. In many cases, the transmittance is not as high as it could possibly be because of the presence of these metal ion impurities which may be present in the raw materials, or which may become entrapped in the glass from the environment during the manufacturing process. In silica glass, these metal ion impurities do not enter the glass silicon-oxygen network, but their electric charge is compensated by the occurrence of non-bridging oxygen ions in the silicon-oxygen network. These non-bridging oxygen ions also contribute to absorption in the deep ultraviolet and vacuum ultraviolet spectral regions. Thus, the resulting structures give broad absorptions in the UV spectral range, thereby decreasing the glass transmittance.

15 Although details of the reaction are not fully understood, without intending to be bound by theory, the following may be proposed. The decrease in UV transmittance may be associated with a charge transfer-type absorption between the impurity metal ions and their non-bridging oxygen ligands, with their energy level difference lying within the energy band gap of the glass. Thus, one method of improving the transmittance of the glass is by reducing the charge transfer absorption between the metal ion impurities and the non-bridging oxygen in the glass.

20 The resulting reaction with hydrogen reduces the oxidation state of the metal ion impurities and converts the non-bridging oxygen into SiOH groups as described by the following equations:



30

where e^- is an electron and M^{+n} is an impurity metal ion such as Fe^{3+} and other transition

metal ions for examples.

The increased transmittance results because either or both (a) the lowering of the energy level of the OH species relative to the O⁻ and (b) the raising of the energy level of the reduced species of the metal impurity ion. The ability to reduce will depend on the specific ion in question; for example, common multi-valent ions such as Fe³⁺ will be easier to reduce than Na⁺.

The amount of hydrogen and/or deuterium that can be diffused into the glass is dictated by the concentration in the ambient. The uniform concentration throughout the sample was assured by using the results of the diffusion equation with the diffusion coefficient of H₂ in SiO₂ given by:

$$D = (5.65 \times 10^{-4}) \exp[-10.4/RT]$$

where, D= coefficient of diffusion

$$R = 1.987 \times 10^{-3} \text{ kcal/mol } ^\circ\text{K}$$

$$T = \text{temp, } ^\circ\text{K}$$

The duration of the treatment with hydrogen and/or deuterium is calculated by the following equation:

$$t = L^2/4D$$

where, L=thickness of the glass; and D is as defined above to assure that 90% of the ambient concentration was present at the midpoint of the sample.

The required amount of hydrogen and/or deuterium will depend on the number of impurity ions and non-bridging oxygen ions present in the given glass. There is no requirement for excess molecular hydrogen and/or deuterium.

We have found that the benefits to be derived from the present invention are greater for those glasses having large numbers of impurity metal ions and non-bridging oxygen ions, than for glasses having relatively fewer impurity metal ions and non-bridging oxygen ions. Since the incremental improvement in transmittance is relatively less for the latter, the ability to observe improvements in the transmittance of glasses having very few non-bridging oxygen and metal ion impurity defects, will depend on the sensitivity of the measuring instrument.

Some high purity fused silica glasses contain a high concentration of =SiOH as a result of the glass making process employed in the production of these glasses. This

high initial concentration of $\equiv\text{SiOH}$ makes it difficult to follow, spectroscopically, the formation of new $\equiv\text{SiOHs}$ resulting from the hydrogen treatment. The use of deuterium, however, makes it possible to determine the amount of $\equiv\text{SiOD}$ formed through the process. Increases in $\equiv\text{SiOD}$ can then be correlated to improvements in UV transmittance.

In order to make the estimate of SiOD concentration as quantitative as the estimate of SiOH , the following procedure can be performed. The absorption peak assigned to molecular deuterium, D_2 is located at 2975 cm^{-1} . We have previously found that molecular hydrogen can be identified in the infrared when it is in sufficiently high concentrations, at 4136 cm^{-1} . Using a theoretical isotope substitution ratio of 1.39, D_2 should come at 2975 cm^{-1} . Referring to Figure 1, for example, Example 1, this peak is found. The extinction coefficient of D_2 is estimated to be that of H_2 , $\sim 0.26\text{ liters/mole cm}$, giving a final concentration of D_2 in Example 3 as approximately 2.3×10^{19} molecules / cc SiO_2 . From the previous work, hydrogen concentration at this loading pressure is calculated to be 2.8×10^{19} molecules / cc SiO_2 . This excellent agreement suggests that the use of the SiOH extinction coefficients for estimating SiOD concentration is justified.

A thermal scrambling of D for H by the reaction



can be ruled out as the source of $\equiv\text{SiOD}$ formed. This is determined by subtracting the overtone band of $\equiv\text{SiOH}$ (4520 cm^{-1}) in the reference sample from the same band in the deuterated samples. This is illustrated in Figure 2. As shown, there is no change in $\equiv\text{SiOH}$ concentration with high pressure deuterium treatment. The $\equiv\text{SiOD}$ found in the IR experiment can then be related to the reaction of D_2 with non-bridging oxygens, the result of which is seen in increased UV transmittance.

We have found that increases in initial transmittance (T_0) are observed, for the most part, only when the glass has relatively low transmittance to begin with. The following examples were carried out using essentially 100% hydrogen and deuterium gases. However, suitable mixtures of hydrogen and inert gases such as argon or

nitrogen, for example, 4% hydrogen and 96 % nitrogen, may also be used. Other gaseous reducing agents such as carbon monoxide can also be used. Hydrogen and deuterium have the advantage that they can more readily be diffused into the glass to produce the desired reactions.

5

EXAMPLES

The examples below verify the improvement of transmittance by hydrogen treatment and also describe the mechanism by which this improvement is achieved.

10 Example 1: In order to verify the improvement of initial transmittance by high pressure hydrogen treatment, two pieces of 1 X 1.5 X 2 cm fused silica containing about 900 ppm of OH were deuterium treated at 90 atm, and 350 °C, for 24 days. UV spectra, IR spectra and IR spectral subtractions were then obtained for the deuterium-treated samples (T1 and T2), and compared with those of the untreated sample (R1).

15 Figure 3a shows the UV transmittance spectra of untreated glass and for the two deuterium treated samples, T1 and T2, from 180 to 220 nm. The spectra were normalized to give 100% transmittance at 220 nm. The transmittance of each sample at 193 nm were 0.9262 for reference sample R1, 0.9363 for the first deuterium-treated sample T1, and 0.9397 for the second deuterium-treated sample, T2. From the UV
20 curves and from the transmittance numbers it is seen that there is a small but measurable improvement in transmittance in the UV after deuterium treatment. Figure 3b show the spectra for all three samples in absorbance. As shown, the initial absorbance of the reference sample R1 was 0.0329, compared to 0.0284 and 0.0269 for deuterium-treated samples T1 and T2 respectively.

25 Figure 4 shows the infrared spectra from 5000 to 2000 cm^{-1} of the two deuterated samples and a reference glass (R1). For all the samples, the peak at high wavenumbers ($\sim 4520 \text{ cm}^{-1}$) can be attributed to an overtone of an OH and $=\text{SiOH}$ combination band. The strong band at about 3600 cm^{-1} is the $=\text{SiOH}$ stretch, typically used for determination of OH concentration. The band at 4520 cm^{-1} can also be used to
30 calculate SiOH in thick samples or samples with high OH content.

The subtractions of the untreated reference glass from the deuterium treated glasses from 3200 to 2500 cm^{-1} are shown in Figure 1. The subtraction spectra clearly show the presence of a peak at 2720 cm^{-1} . This peak is attributed to SiOD which is the result from the deuterium treatment of the glasses, by the reaction described above. The shift, at 2720 cm^{-1} , agrees well with what would be expected from isotopic substitution of H for D.

It is seen that the sample that exhibits a greater increase in initial UV transmittance also has more SiOD (sample T2). A plot of SiOD vs. change in absorbance for the three samples is presented in Figure 5. The line shows a modest agreement of SiOD formation with increased UV transmittance.

The results of the increased transmittance with formation of SiOD are in accordance with the observation that glass having poor initial transmittance benefits more from hydrogen treatment than does glass having high initial transmittance.

Example 2: Hydrogen/deuterium impregnation of fused silica samples was carried out, at 600°C, 1 atm, for 48 hours. This time was chosen in accordance with the diffusion equation for hydrogen in silica at 600°C for a 1 cm thick piece. Vacuum UV spectra (Figures 6a and 6b), recorded before and after the low pressure hydrogen treatment show a significant increase in initial transmittance as a result of the treatment. As in Example 1 and Figures 1 through 5, we have again shown that initial transmittance is improved by hydrogen treatment. This result shows that high pressure hydrogen treatment is not necessary in order to improve initial UV transmittance in fused silica.

Also, in this example, samples of Corning glass codes 7940 and 7980 were subjected to 600°C, 48 hours, 1 atm hydrogen treatment. Table 1 compares the transmittance/cm of the glasses at 210 nm and 248 nm before and after this hydrogen treatment.

Table 1. Transmittance/cm before and after hydrogen

Sample	210 nm	248 nm
	Before/After	Before/After
1	86.7/90.0	90.0/91.7
2	79.5/89.9	84.5/91.4
3	80.1/90.2	86.4/91.9
4	89.7/90.4	91.4/92.0
5	86.6/89.3	90.2/91.4
6	82.0/88.7	88.0/91.4
7	81.5/87.3	88.6/91.6
8	84.4/86.9	88.3/89.7

Example 3. In this example, silica was made by the densification of a powder precursor and subsequently treated in hydrogen at 600°C as above. The ultraviolet transmittance of the glass was measured before and after hydrogen treatment. Transmittance/cm and hydroxyl content, as determined by infrared, of the sample before and after hydrogen treatment are shown in Table 2 below.

Table 2. Transmittance and OH of powder process glass.

	210 nm	248 nm	OH (wt, ppm)
Before	70.9	82.1	<1
After	76.0	88.9	4

The present invention can be applied to any glass intended for use in the ultraviolet range to improve the initial transmittance. In our preferred embodiment, the method is applied to fused silica produced from silicon tetrachloride or a halide-free polymethylsiloxane. Preferred polymethylsiloxanes include, hexamethyldisiloxane, polymethylcyclsiloxane, and mixtures of these. In one particularly useful embodiment, the fused silica is made from a polymethylcyclsiloxane such as, octamethylcyclotetra-siloxane, decamethylcyclopentasiloxane, hexamethylcyclotrisiloxane, and mixtures of these.

In addition to the embodiments discussed above, it will be clear to persons skilled in the art that numerous modifications and changes can be made to the above invention without departing from its intended spirit and scope.

CLAIMS:

1. Method of improving the transmittance of optical glass by treating the optical glass with a gas selected from the group consisting of hydrogen and deuterium.
- 5 2. The method of claim 1, wherein the transmittance is improved by subjecting the optical glass to the gas at a temperature and for a duration sufficient to cause the gas to diffuse into the optical glass.
- 10 3. The method of claim 1, wherein the gas is hydrogen.
4. The method of claim 3, wherein the optical glass is 1 cm in thickness and is subjected to hydrogen at a temperature of 600 °C, and for duration of 48 hours.
- 15 5. The method of claim 3, wherein the optical glass is subjected to hydrogen at a pressure of 90 atm and a temperature of 350 °C.
6. The method of claim 1, wherein the optical glass is fused silica.
- 20 7. The method of claim 6, wherein the fused silica is formed from SiCl_4 .
8. The method of claim 6, wherein the fused silica is formed from a halide-free polymethylsiloxane.
- 25 9. The method of claim 8, wherein the polymethylsiloxane is selected from hexamethyldisiloxane, polymethylcyclotrisiloxane, and mixtures of these.
10. The method of claim 9, wherein the polymethylcyclotrisiloxane is selected from the group consisting of octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, hexamethylcyclotrisiloxane, and mixtures of these.
- 30

11. The method of claim 1, wherein the optical glass comprises metal ion impurities and non-bridging oxygens.

5

12. The method of claim 11, wherein the metal ion impurities comprise transition metal ions.

13. The method of claim 12, wherein the transition metal is iron.

10

14. The method of claim 11, wherein the optical glass is further characterized by a charge transfer absorption between the metal ion impurities and the non-bridging oxygen.

15

15. The method of claim 14, wherein the transmittance is improved by reducing said charge transfer absorption.

1 / 4

FIG. 1

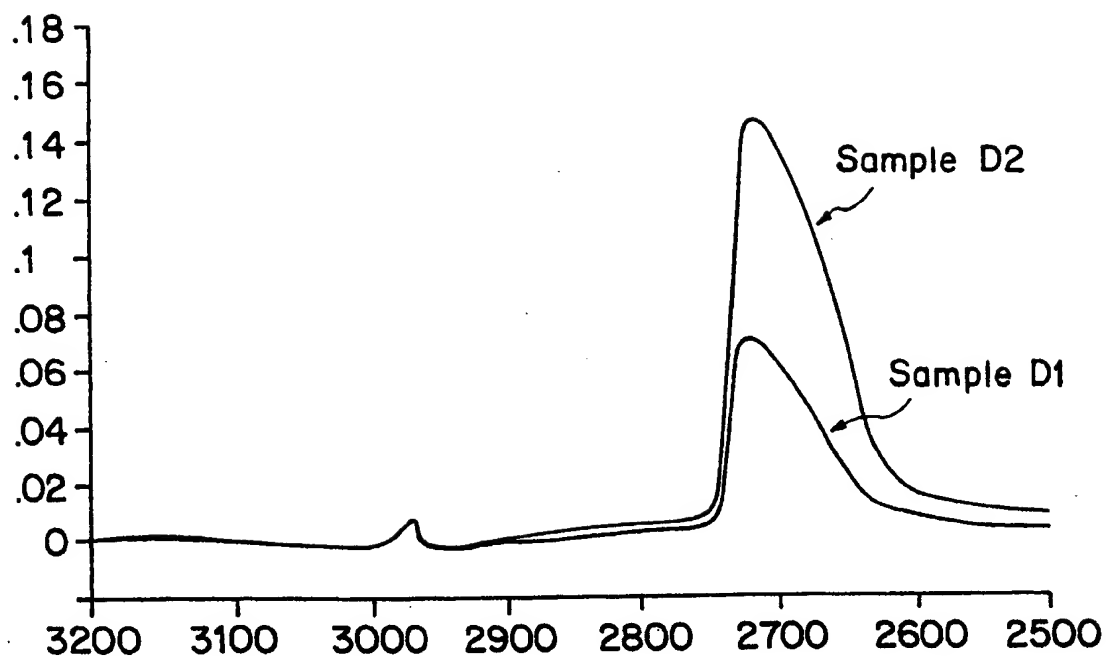
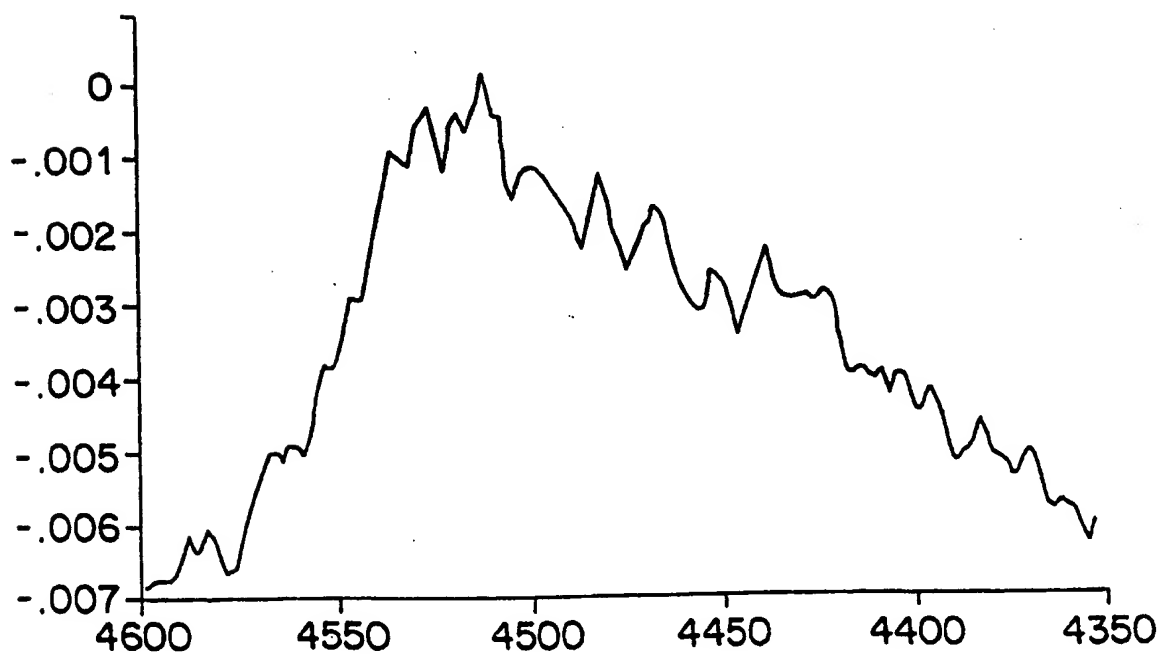


FIG. 2



2 / 4

FIG. 3A

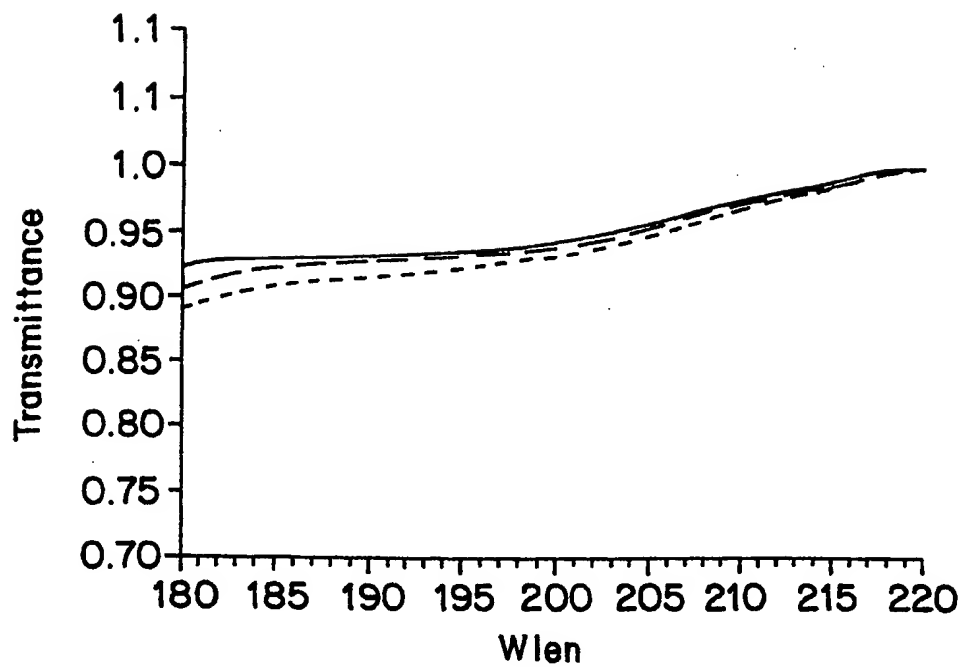
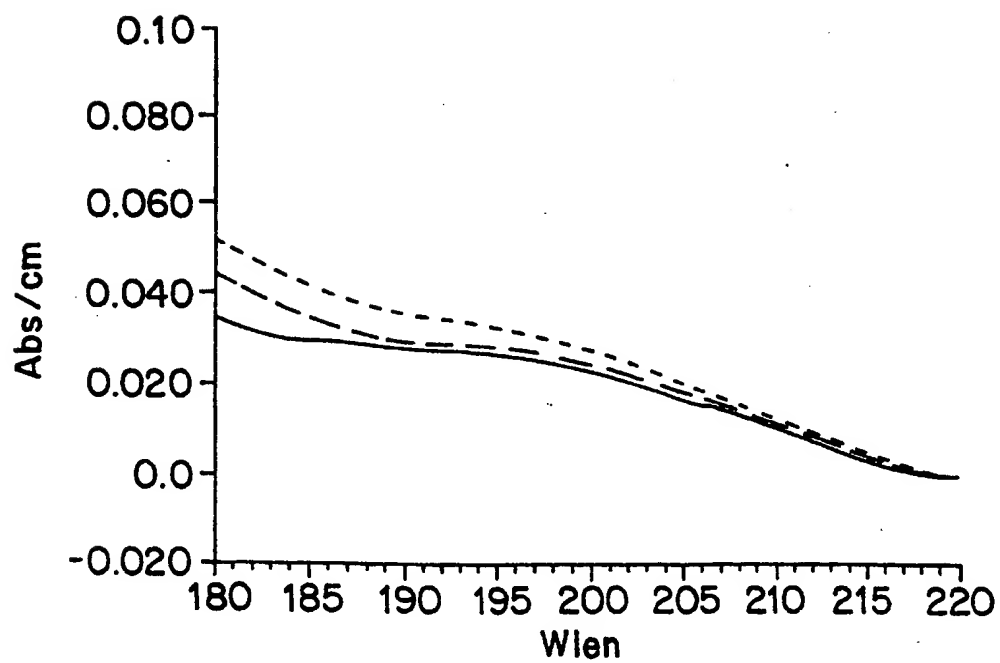


FIG. 3B



3 / 4

FIG. 4

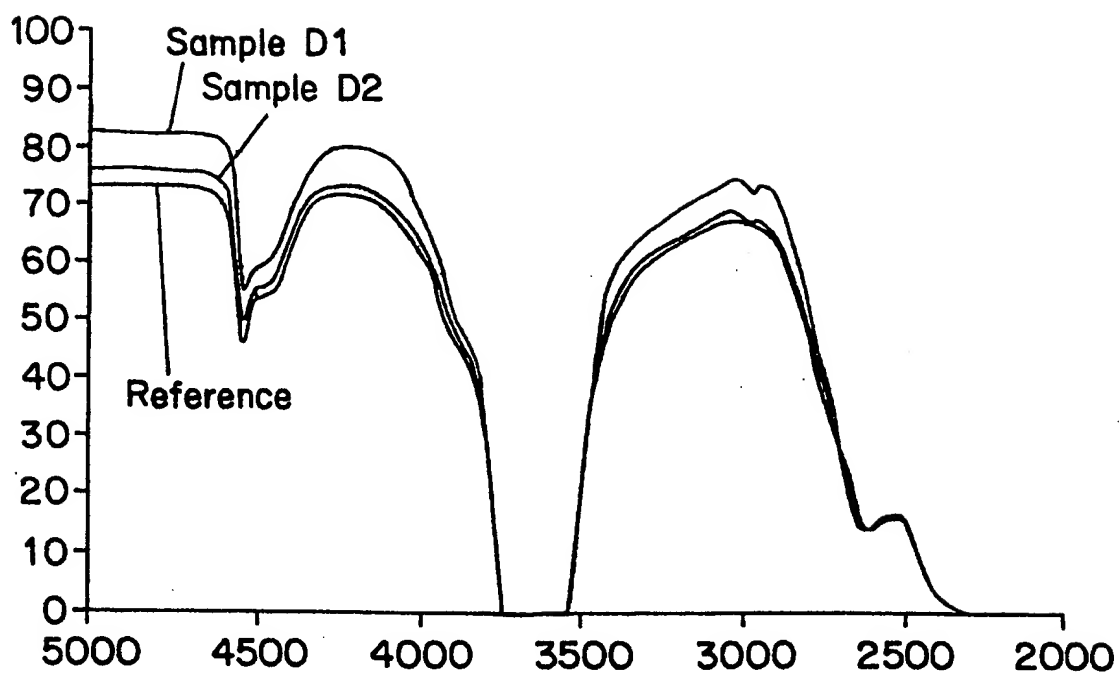
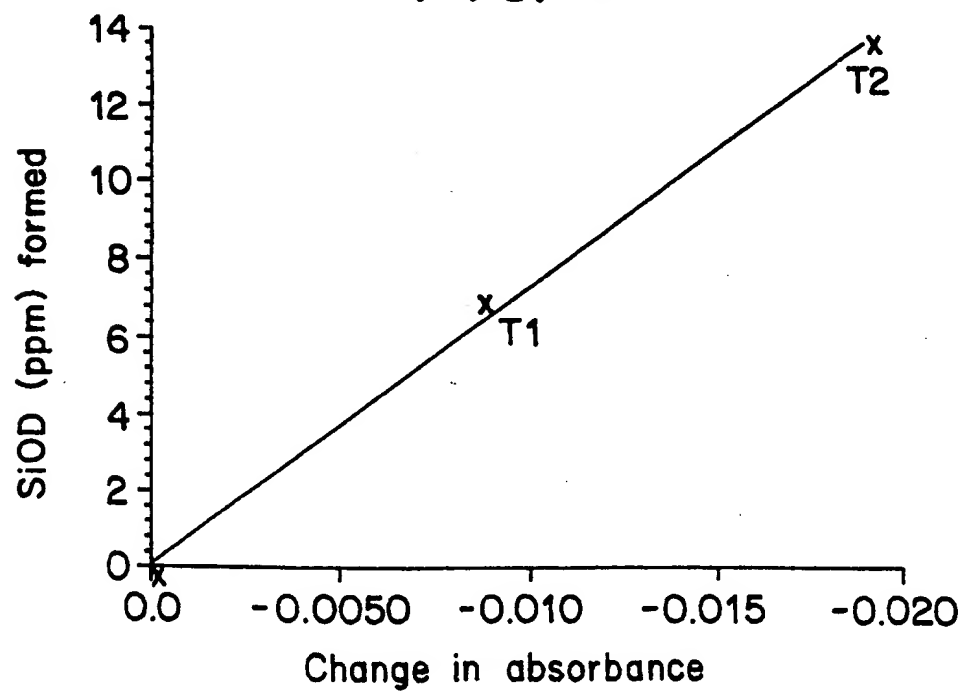


FIG. 5



4 / 4

FIG. 6A

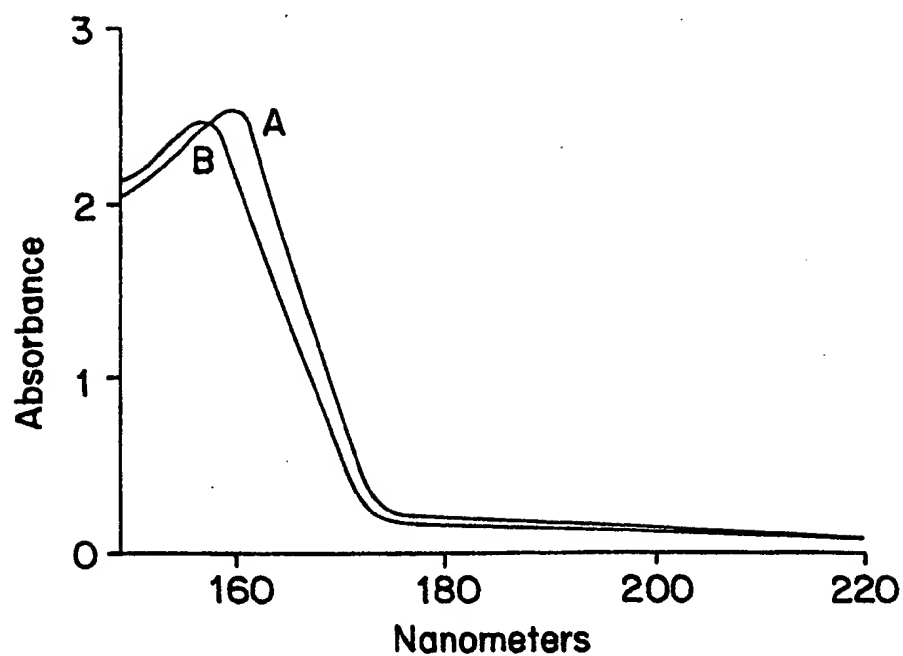
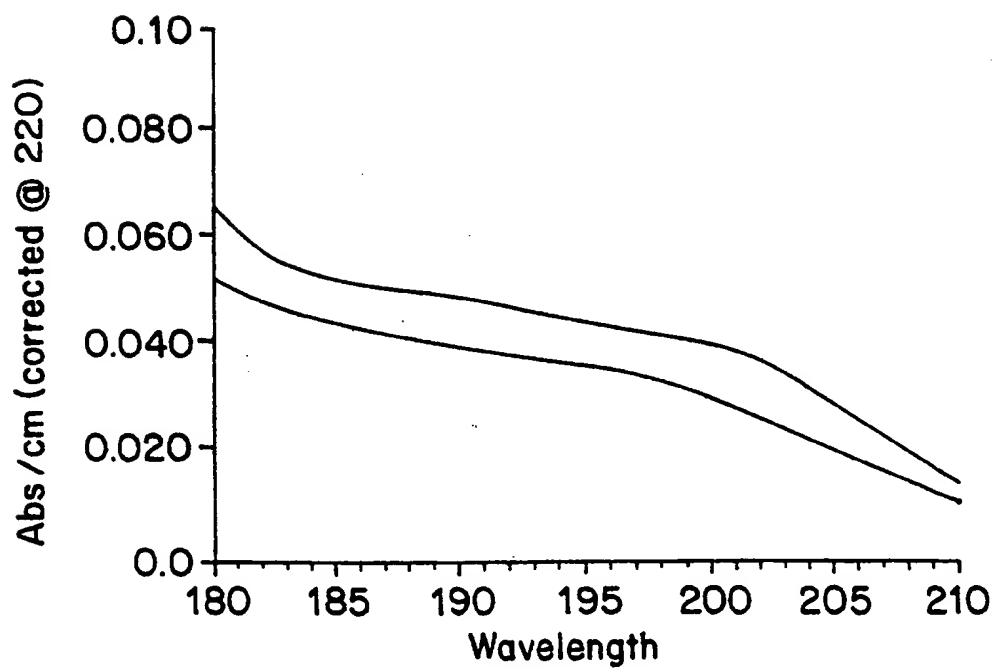


FIG. 6B



INTERNATIONAL SEARCH REPORT

I. National application No.
PCT/US97/03100

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : CO3B 20/00; CO3C 21/00

US CL : 65/30.1, 32.1

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 65/17.4, 17.5, 17.6, 30.1, 30.13, 32.1, 394, 400, 421

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAS

search terms: h2, hydrogen, dop###, silica, quartz, transmi?, absorb####, absorp####

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,086,352 A (YAMAGATA ET AL) 04 February 1994,	1-7, 11-15
---	col. 2, line 60 to col. 3, line 13, col. 6, lines 53-64, col. 9,	---
Y	line 45 to col. 10, line 54, col. 15, lines 23-47.	8-10
Y	US 5,043,002 A (DOBBINS ET AL) 27 August 1991,	8-10
	Examples 2 and 4.	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"G"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

25 APRIL 1997

Date of mailing of the international search report

07 MAY 1997

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

DONALD CEJA

Telephone No. (703) 308-5551